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# Acceleration of galvanic lead solder corrosion due to phosphate

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# article info

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# abstract

Although orthophosphate is often effective in reducing lead corrosion, bench-scale tests revealed cases in which even high doses of orthophosphate (1–3 mg/L P) in potable water increased lead and tin release from simulated soldered copper joints. Phosphate increased the galvanic current between tin and copper plumbing materials, especially in water with less than 10 mg/L  $SO_4^{2_1}$  and when the percentage of the anodic current carried by  $SO_4^{2_1}$  ion was less than 30% Tin release was increased more than lead release from 50:50 Pb–Sn solder in these circumstances.

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#### 1. Introduction

# 1.1. Lead solder chemistry

Lead contamination of potable water due to galvanic attack of Pb–Sn solder was first demonstrated by Oliphant [1] and Gregory [2], who also discovered high and persistent galvanic currents between copper pipe and lead solder when the chloride-to-sulphate mass ratio (CSMR, or mg/L Cl<sup>-1</sup> divided by mg/L SO<sub>4</sub><sup>2-1</sup>) of the water was above about 0.5. Other work by Edwards et al. [3] found more exceedances of the United States Environmental Protection Agency (USEPA) Lead and Copper Rule (LCR) when the CSMR was greater than 0.58. Recent work by Nguyen et al. [4] used theoretical transport considerations to identify a critical CSMR of 0.77, above which galvanic attack on lead solder would be expected to increase markedly. There were also several instances in which elevations of the CSMR above these thresholds increased the LCR 90th percentile lead and caused lead poisoning of children [5–8].

Very corrosive microenvironments with high levels of chloride and low pH (e.g., 2.5) can form at lead solder anode surfaces due to galvanic corrosion between lead solder and copper pipe, perpetuating very high rates of lead corrosion [9]. However, higher alkalinity is expected to buffer pH drops associated with galvanic corrosion at lead anode surfaces [10], and higher pH values may also decrease lead solubility [11–13]. Lead oxides, which are well known to form protective scaling on lead surfaces, do not typically

#### 1.2. Effect of phosphate on lead

In low alkalinity water, the optimal pH for orthophosphate inhibition of uniform lead corrosion is between 7.3 and 8 [13,17]. Orthophosphate has been a very effective inhibitor of lead leaching to water in many cases [2,11,17–20]. However, Oliphant [1] measured no decrease in the galvanic current between lead solder and copper when orthophosphate was dosed in pH 7.4–8.5 water, although the resulting impact of orthophosphate on lead in water was not measured. Thus, prior work suggests that galvanic couples may respond differently to phosphate dosing.

Equilibrium modelling can predict the solubility when lead phosphate is the controlling solid over the pH range 3–6 expected at the lead solder anode surface (Fig. 1). For example, 56 Ig/L soluble Pb is present at equilibrium in water at pH 6 with 1 mg/L orthophosphate as P. However, if the pH decreased to 4, which can occur at lead solder surfaces during galvanic corrosion [9], the predicted soluble lead would increase by 370 times to 21 mg/L Pb. Clearly, soluble lead is expected to increase rapidly if the pH at the lead solder anode surface drops below about pH 4.6, even in the presence of orthophosphate corrosion inhibitor and lead phosphate (Pb<sub>3</sub>PO<sub>4</sub>) surface scale.

Bulk water concentrations of sulphate are not expected to significantly alter the soluble lead concentration. However, if sulphate concentrated at the lead anode surface [9] 20 times from 10 mg/L  $\mathrm{SO}_4^{21}$  in the bulk water to 200 mg/L  $\mathrm{SO}_4^{21}$  at the anode, lead sulphate solids could limit the soluble lead to 4 mg/L Pb in the microlayer of pH 4 water at the lead surface (Fig. 1). This could reduce lead leaching to water. Recent work with low sulphate (<20 mg/L

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form on Pb–Sn solder surfaces unless the surface becomes severely depleted of tin [14–16].

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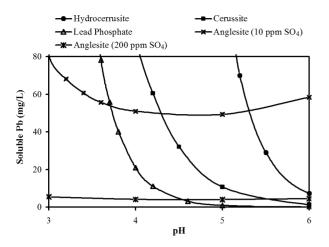


Fig. 1. Equilibrium soluble Pb(II) between pH 3 and 6 for water with 20 mg/L alkalinity as  $CaCO_3$  when anglesite, hydrocerrusite, cerrusite, or lead phosphate is the dominant solid. The modelled orthophosphate concentration was 1 mg/L P.

 $SO_4^{2_{\gamma}}$ ) and low alkalinity water demonstrated that lead concentrations reached 157 mg/L Pb or higher near lead anode surfaces [9].

# 1.3. Tin phosphate chemistry

When tin metal corrodes, Sn(II) is first dissolved from tin metal, and the tin metal eventually completely passivates when Sn(II) at the metal surface oxidizes to Sn(IV) and  $SnO_2$  [21,22]. Tin changes from passive to active corrosion at pH 4–5 [23]. Furthermore, Awad [24] found that phosphate can corrode tin, hypothesizing that tin phosphate complexes formed. Later work by others reported formation constants for various tin phosphate complexes [25], and other tin complexes can form with hydroxide and chloride [26]. In one study with 3100 mg/L P,  $SnOH^+$  and tin phosphate complexes were thought to form [27,28]. Tin carbonate complexes have not been reported [29].

Equilibrium modelling demonstrates the hypothetical extent of tin phosphate complex formation assuming that reported complexation constants are accurate (Fig. 2). Specifically, if 5 mg/L Sn(II) was released to the water, the soluble tin in water containing 3 mg/L P would be 85  $l\,$ g/L, or 110 times more soluble tin than expected in water with no phosphate (0.76  $l\,$ g/L). A large portion of the released tin would precipitate at equilibrium and form scale in either case. The addition of phosphate also slightly buffers the pH drop associated with the Lewis acidity of tin (Fig. 2).

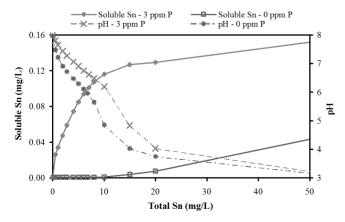


Fig. 2. Equilibrium soluble Sn and pH due to release of Sn(II) at anode surfaces. Alkalinity of the water was 8 mg/L as CaCO<sub>3</sub>.

The objective of this work is to identify the mechanisms by which phosphate can increase Pb–Sn solder corrosion in building plumbing systems, and to investigate the practical impact of orthophosphate on lead solder corrosion in simulated plumbing joints.

#### 2. Materials and methods

## 2.1. Experimental apparatus and procedure

#### 2.1.1. Macrocells

Simulated joints were prepared with pure tin wires and copper pipes [9] to track galvanic corrosion occurring between the two metals. Each macrocell was constructed using a 19-mm diameter copper pipe (310-mm length) and a 13-mm diameter copper pipe (64-mm length), connected by clear Tygon tubing with a 2-mm gap separation between the pipes. A pure tin wire was inserted through the centre of a silicone stopper, and then the stopper with wire was inserted into the 13-mm diameter copper pipe. Water was changed in the macrocells three times per week (Monday, Wednesday, and Friday) by transferring the stagnant water from the pipes into collection bottles for metals analysis and refilling the test pipes with freshly prepared water ("dump-and-fill" method [5]). Tests were conducted in triplicate.

# 2.1.2. Soldered 19-mm pipes

Type M 19-mm diameter copper pipes (22-mm outer diameter, 0.88-mm wall thickness) were cut into 305-mm lengths, and one end of each pipe was dipped in molten 50:50 Pb-Sn solder (50% Pb and 50% Sn by weight) with a depth of 29 mm. The pipes were filled with test water, closed on both ends with silicone stoppers, and tested in triplicate. Water was changed in the pipes three times per week using a "dump-and-fill" method [5].

# 2.1.3. Galvanic solder coupons

A 25-mm length of 3-mm diameter 50:50 Pb—Sn solder was placed on the inner edge of a 25-mm length of 13-mm diameter copper coupling [30]. The galvanic lead solder—copper coupons were exposed to 100 mL of each test water in glass containers and tested in triplicate. The water was changed using a "dump-and-fill" protocol [5] twice per week (e.g., Monday/Thursday), and weekly composite samples were collected for each water condition at the end of each week. The stagnation time was selected to represent long stagnation times that can occur during weekends in building plumbing and that allow the formation of microclimates that are detrimental to lead corrosion [9].

# 2.1.4. Galvanic solder end caps

Simulated joints were prepared by assembling a 24-mm diameter copper end cap and a 51-mm length of 19-mm diameter copper pipe [4]. A 152-mm length of 3-mm diameter 50:50 Pb–Sn solder was then melted to form a layer of solder at the bottom of the inner surface of the end cap. The galvanic lead soldered copper end caps were placed into glass containers and exposed to approximately 500 mL of each test water in triplicate. The headspace was minimized by filling the glass containers to capacity to limit dissolution of carbon dioxide (CO<sub>2</sub>) from the air during stagnation. The water was changed using a "dump-and-fill" protocol twice per week [5], and weekly composite samples were collected for each water condition at the end of each week.

# 2.2. Water chemistry

The case studies presented herein represent water from communities in the United States in which increased lead release was observed at bench-scale due to orthophosphate addition. The water conditions are described in this section and in Table 1.

#### 2.2.1. Macrocells

Treated water, but prior to disinfection, was received at Virginia Tech from a water utility. Reagent grade chemicals were added to the water including orthophosphate corrosion inhibitor, bicarbonate, sulphate, disinfection with free chlorine, and acid or base for final pH adjustment (Table 1). The water from the treatment plant contained 4 mg/L CI, and all test water exposed to the macrocells was dosed with 10 mg/L CI after Week 14 of the study to simulate a portion of the chloride that entered the water due to the hypochlorite generator brine leak.

The pH was adjusted with either 0.1 M NaOH or 0.1 M  $\rm HNO_3$  to the target value of pH 7.3 or 9.2. All water was also chlorinated at a dose of 2 mg/L  $\rm Cl_2$ . Orthophosphate was dosed from sodium phosphate (Na<sub>2</sub>HPO<sub>4</sub>). Alkalinity was adjusted with sodium bicarbonate (NaHCO<sub>3</sub>). Chloride and sulphate were added from sodium chloride (NaCl) and sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), respectively.

# 2.2.2. Soldered 19-mm pipes

Water in this test had a CSMR of 1.2, alkalinity of 34 mg/L as CaCO $_3$ , 2 mg/L Al (aluminium solids), 0.3 mg/L TOC from pre-chlorinated NOM, and 1.25 mg/L NH $_3$ –N (Table 1). The pH was adjusted to 7.0 or 9.5 ± 0.2 with NaOH or HCl prior to exposure to the soldered pipes. Chloramine concentrations (0 or 5 mg/L Cl $_2$ ) and orthophosphate (0 or 3 mg/L as P) were varied in the test water. Chemicals were added as reagent grade salts to distilled and deionized water.

# 2.2.3. Galvanic solder coupons

The 50:50 Pb–Sn soldered copper coupons [30] were exposed to a utility water with a typical alkalinity of 8 mg/L as CaCO $_3$  and CSMR of about 4 (Table 1). To simulate a brine leak that occurred from the on-site hypochlorite disinfectant generator, 9 mg/L Cl from NaCl was added to the water after Week 17 of the study, increasing the CSMR to 8.5. Orthophosphate (NaH $_2$ PO $_4$ ) at a dose of 1 mg/L P and 20 mg/L alkalinity as CaCO $_3$  from NaHCO $_3$  were also evaluated. The final test waters were adjusted to match the final pH (7.3) and disinfectant dose (2 mg/L free chlorine as Cl $_2$ ) used at the treatment plant (Table 1). Chemicals were added as reagent grade salts.

#### 2.2.4. Galvanic solder end caps

Water was prepared with 0–120 mg/L alkalinity as  $CaCO_3$  from NaHCO $_3$ . Chloride was added at a concentration of 10 mg/L Cl (from NaCl) for the first 6 weeks and reduced to 2 mg/L Cl for Weeks 7–9 (Table 1) to test the effects of two chloride levels. The final pH was adjusted to pH 7.5 or 8.5 by dosing NaOH or  $CO_2$ . Chemicals were added as reagent grade salts to distilled and deionized water.

Table 1 Water chemistry of test waters.

#### CSMR<sup>a</sup> Alkalinity Orthophosphate<sup>b</sup> Disinfectant Test (apparatus) Cl1 (mg/L) SO<sub>4</sub><sup>2</sup> (mg/L as CaCO<sub>3</sub>) (mg/LP) (mg/L as Cl<sub>2</sub>) (mg/L SO<sub>4</sub>) Mechanism (macrocells) 3-12 3-4.7 8-58 Free chlorine (2 mg/L) 4 or 14 7.3 Case Study 1 14 1.2 7 or 9.5 3 Chloramines<sup>c</sup> (0 or 5 mg/L) (soldered 19-mm pipes) 8 (typ.)d or 17 7.3 Free chlorine (2 mg/L) Case Study 2 2 4 (typ.) or 8.5 8 (typ.) or 20 1 or 1.8 (galvanic lead solder coupons) Case Study 3 10 or 2 0 0-120 7.5 None (galvanic lead solder end caps) (after Week 5)

# 2.3. Analytical methods

Total metals release was quantified after acidifying water samples with 2% nitric acid for at least 24 h. Lead, tin, chloride, and sulphate concentrations in the bulk water were measured using an inductively coupled plasma mass spectrometer (ICP-MS) in accordance with Standard Method 3125-B [31]. Concentrations of chloride and sulphate were cross-checked using DIONEX DX-120 ion chromatography according to Standard Method 4110 [31]. The pH in the bulk water was measured with an Accumet electrode in accordance with Standard Method  $4500\text{-H}^{+}$  B [31]. Electrochemical measurements between the copper pipes and the tin wires in the macrocells were conducted using RadioShack multimeters with 100 O resistance. Galvanic current measured between the anode (tin wire) and the cathode (copper) is an indicator of galvanic corrosion [32].

#### 3. Results and discussion

The adverse effects of phosphate on lead leaching were quantified by comparing lead release to water with and without phosphate as follows:

Pb ratio 
$$\frac{1}{2}$$
 Concentration of Pb in water with phosphate  $\frac{1}{2}$  The open concentration of Pb in water without phosphate  $\frac{1}{2}$ 

If the calculated ratio is less than 1, dosing phosphate to that specific water mitigated lead corrosion, whereas a ratio greater than 1 indicates that phosphate increased lead release. A similar calculation was done for tin. The calculated ratios were compared to the predicted percentage of the anodic corrosion current carried by transport of sulphate ( $SO_4^{2_1}$ ) ions through solution toward the lead solder anode as described elsewhere [3,4]. There was a tendency for phosphate to increase lead release if the sulphate concentrations were low (<10 mg/L  $SO_4$ ) or if less than 30% of the carrying current was carried by sulphate ions (Fig. 3). In some situations, the addition of phosphate increased lead release to the water by a factor of 600% (i.e., Pb ratio of 6) (Fig. 3). Moreover, the detrimental effect of phosphate on tin was even more dramatic, with as much as 14 times more tin in the water after addition of the orthophosphate corrosion inhibitor (Fig. 3). These results suggest that an attack on the tin phase in 50:50 Pb-Sn solder alloy may be important to explaining the effect of phosphate on solder corrosion.

### 3.1. Mechanism of phosphate attack

To understand the increased dissolution of lead-tin solder due to orthophosphate, which was observed in some situations (Fig. 3), a study was conducted to investigate the galvanic corrosion of pure tin wire connected to copper pipe. Specifically, water from a utility was subjected to a range of alkalinity, pH, and sul-

 $<sup>^{</sup>a}$  Chloride-to-sulphate mass ratio (CSMR) provided as mg/L Cl $^{ ext{ iny per mg/L SO}_4^{2_{1}}}$ 

b Dose(s) evaluated in studies, excluding 0 mg/L P.

<sup>&</sup>lt;sup>c</sup> Chloramines dose of 4:1 mg Cl<sub>2</sub>/mg NH<sub>3</sub>-N.

d Typical (typ.).

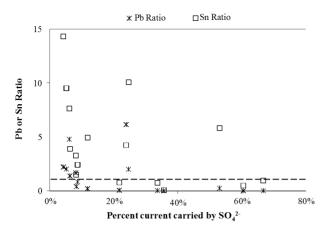


Fig. 3. Lead (Pb) and tin (Sn) ratios for solder (metal concentration with phosphate divided by metal concentration without phosphate, Eq. (1)) as a function of the percentage of current carried by  $SO_4^{2\gamma}$  ion. The dashed line at a ratio of 1 indicates the level at which phosphate had no effect on lead or tin release. Data were reprocessed from previous studies [30,34].

phate treatment strategies with and without orthophosphate (Table 1) and was tested using the macrocell apparatus [9]. The galvanic current and tin concentration in water were tracked.

In half of the test water conditions, the galvanic current increased with the addition of 1 mg/LP, although the results were statistically significant only for the water with 10 mg/L alkalinity as CaCO<sub>3</sub> added (Fig. 4). However, the tin concentrations increased 3–16 times due to the addition of 1 mg/L P for all of the water conditions (Fig. 4), and the results were significantly different with 95% confidence for all but two waters (water amended with 10 mg/L SO<sub>4</sub><sup>27</sup> or 50 mg/L alkalinity as CaCO<sub>3</sub>). Specifically, in the utility water with 18 mg/L alkalinity as CaCO<sub>3</sub>, the tin concentration increased 16 times from 40 Ig/L Sn to 670 Ig/L Sn by adding 1 mg/L P (Fig. 4). Concurrently, the galvanic current increased 4.5 times from 0.6 to 2.8 IA (Fig. 4). The trend in tin concentrations agreed with the predictions based on the current measurements and Faraday's law (results not shown), although a large portion of the oxidized tin likely accumulated in the scale [9]. Similar observations of higher current and tin concentrations in water with phosphate were noted in tests with pure tin wire polarized  $\neg$  0.2 V vs.  $E_{ref}$  with a platinum counter electrode (results not shown), and there was high variability in the galvanic current measurements among replicates. These higher tin concentrations and galvanic currents due to the orthophosphate addition in water with low sulphate (3 mg/L  $SO_4^{2_1}$ ) are consistent with previous findings (Fig. 3). Calculations indicate that between 7% and 21% of the anodic current was carried by sulphate in most of these test waters.

Clearly, the galvanic current sacrificing the Pb–Sn solder anode was increased due to orthophosphate in some cases, which in turn translates to lower pH and higher concentrations of aggressive anions such as Cl<sup>-1</sup> at the Pb–Sn solder surface [9].

Moreover, the increased lead and tin corrosion of solder at joints can decrease its integrity and cause premature failure in home plumbing [33,34]. The specific factors causing the increase in galvanic current were not identified in this work. However, it is possible that phosphate slowed the transition of Sn(II) to less soluble and more protective Sn(IV), thereby increasing the time for passivation of the metal and the amount of soluble tin in water containing phosphate. Future work is needed to confirm this mechanism.

### 3.2. Case studies where phosphate increased lead solder corrosion

The macrocell study demonstrated that tin corrosion increased due to phosphate. Consequently, higher tin concentrations at the

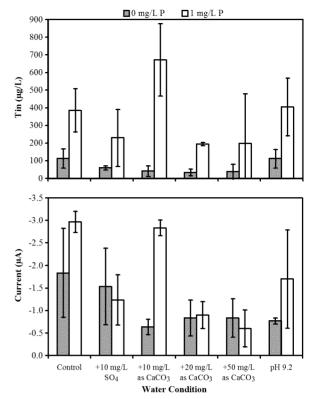


Fig. 4. Total tin in water and galvanic current between pure tin wire and copper pipe in macrocells. The water had a pH of 7.3 and contained 3 mg/L  $SO_4^{S_1}$ , 4 mg/L  $Cl^{\gamma}$ , 8 mg/L alkalinity as CaCO $_3$ , and 2 mg/L free chlorine as  $Cl_2$ , unless otherwise specified. Data points are from Weeks 12 to 14 of the experimental study. Error bars represent 95% confidence intervals.

solder surface and the stronger Lewis acidity of tin compared to lead can promote corrosion and lead release from 50:50 Pb—Sn solder. Although we and others have documented numerous instances where phosphate was effective in inhibiting lead corrosion in potable water distribution systems [11,13,17,18,20], the following studies focus on cases where phosphate increased corrosion of Pb—Sn solder in potable water.

#### 3.2.1. Case Study 1

In one water with an alkalinity of 34 mg/L as CaCO3 and a CSMR of 1.2 (Table 1), lead release from galvanic 50:50 Pb-Sn solder increased as much as 2 times when 3 mg/LP was dosed. Specifically, in pH 7 water with 5 mg/L chloramines as Cl<sub>2</sub>, lead release doubled from 4580 to 9220 Ig/L, but the results were not significant at the 95% confidence level (Fig. 5). However, tin was more affected than lead by phosphate, and the tin concentration significantly increased 3-10 times when 3 mg/L P was added (Fig. 5). In the same water in which the lead concentration doubled (pH 7 and 5 mg/L Cl<sub>2</sub>), tin release increased by an order of magnitude from 110 to 1070 lg/L. Water at pH 7 appeared to be more affected by phosphate than pH 9.5 water (Fig. 5). That is, phosphate increased tin release 7-10 times in pH 7 water, whereas an increase of 3-4 times more tin was observed in water at pH 9.5 due to phosphate. There was no evidence that chloramine disinfectant significantly affected solder corrosion for this water.

In addition to higher lead and tin concentrations, more white particles, which were presumably lead and tin colloidal particles, could be observed in the potable water with orthophosphate compared to the same water with no phosphate (e.g., Fig. 6). In this case study, tin corrosion unambiguously increased due to orthophosphate, which is consistent with observations for pure tin wire (Fig. 4) and in some previous work with 50:50 Pb—Sn solder (Fig. 3).

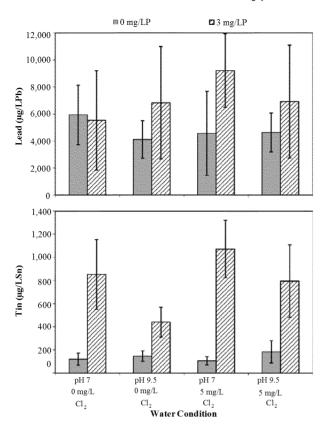


Fig. 5. Lead and tin release from soldered copper pipes exposed to a water with a CSMR of 1.2, alkalinity of 34 mg/L as  $CaCO_3$ , and chloramines disinfectant where indicated. Data are from Weeks 1, 3, 6, and 8 of the study. Error bars represent 95% confidence intervals.

# 3.2.2. Case Study 2

Consistent with expectations from other studies [2,11,13,17, 18,20], orthophosphate decreased lead corrosion of solder coupons for a utility water with 8 mg/L Cl and 8 mg/L alkalinity as  $CaCO_3$  (Fig. 7). However, in the other test water conditions, including water with a higher alkalinity of 20 mg/L as  $CaCO_3$  or chloride concentration of 17 mg/L Cl, lead release increased by 2 times with the addition of 1 mg/L P. The findings were significant at the 95% confidence level for the condition with 20 mg/L as  $CaCO_3$  and 8 mg/L Cl.

Moreover, for the same soldered coupons, tin release increased 2–14 times for all of the test water types due to orthophosphate,

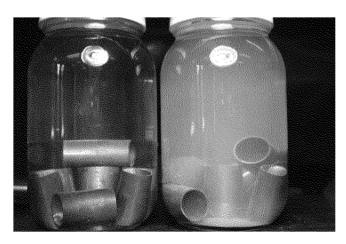


Fig. 6. Example of white colloidal particles released from galvanic lead solder coupons in pH 7 water with orthophosphate (right) compared to the same water without orthophosphate corrosion inhibitor (left).

and the results were significant at the 95% confidence level, with the exception of the water with an alkalinity of 8 mg/L as CaCO3 and 8 mg/L Cl. In the worst case (water with 20 mg/L as CaCO<sub>3</sub> and 17 mg/L CI), adding 1 mg/L P increased tin release by 14 times from 40 lg/L Sn to 580 lg/L Sn (Fig. 7). Furthermore, increasing the alkalinity slightly in this water worsened the effect of phosphate on tin corrosion, even though significant increases in lead corrosion were observed at both alkalinities. Specifically, adding 1 mg/L P to water with an alkalinity of 20 mg/L as CaCO<sub>2</sub> increased tin release 5-14 times, whereas adding phosphate to lower alkalinity water (8 mg/L as CaCO<sub>3</sub>) increased tin release 2-9 times (Fig. 7). Additionally, water with more chloride worsened the effect of phosphate. For example, dosing orthophosphate to water with 8 mg/L Cl increased tin release 2-5 times, while an increase of 9-14 times more tin was measured in water with 17 mg/L CI. In summary, for most of the waters tested in this utility study, phosphate significantly increased tin release from 50:50 Pb-Sn solder, and increases in lead release were also observed.

# 3.2.3. Case Study 3

In water containing 2 mg/L Cl and alkalinity in the range of 0–120 mg/L as  $CaCO_3$ , lead release from soldered end caps increased between 30% and 950% due to phosphate, and the results were statistically significant for all conditions, with the exception of 40 and 60 mg/L alkalinity as  $CaCO_3$  (Fig. 8). For example, lead release increased by a factor of 4 from 270 lg/L Pb to 1170 lg/L in water with 10 mg/L as  $CaCO_3$  when 1 mg/L P was added

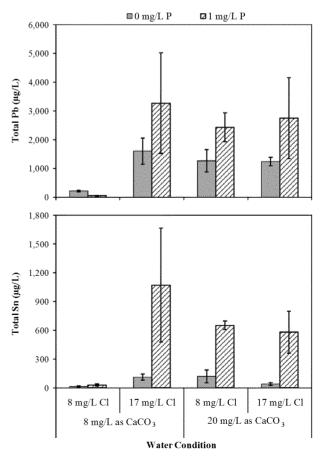


Fig. 7. Effect of phosphate on total lead and tin release from galvanic 50:50 Pb-Sn solder. Data for 8 mg/L Cl was collected during Weeks 12-14 of the study, while 17 mg/L Cl data was from Weeks 18 to 20. Error bars represent 95% confidence intervals.

(Fig. 8). Moreover, higher alkalinity did not reduce the effect of phosphate, although less lead was measured in water with higher alkalinity. For example, lead in water with 120 mg/L as  $CaCO_3$  increased an order of magnitude from 40 to 440 lg/L Pb when phosphate was added. However, much higher alkalinity might mitigate lead corrosion due to buffering and other factors [4].

Completely consistent with the other case studies, the effect of phosphate on tin release was more dramatic than lead, with increases from 65% to more than 2000% more tin in this water when 1 mg/L P was added. Specifically, 1 mg/L P increased tin release by an order of magnitude from 18 lg/L Sn to 190 lg/L Sn in water with 10 mg/L alkalinity as CaCO<sub>3</sub> (Fig. 8). Moreover, the largest impact of phosphate was observed at the highest alkalinity level (120 mg/L as CaCO<sub>3</sub>), in which case tin release increased 20 times from 6 lg/L Sn to 125 lg/L Sn with the addition of phosphate. Phosphate significantly increased tin release for all alkalinity levels at the 95% confidence level, with the exception of water with 5 mg/L as CaCO<sub>3</sub>.

To further compare the relative effect of phosphate on lead and tin release among the alkalinity levels and the two chloride concentrations in this study, the ratio of lead or tin release with phosphate vs. without phosphate (Eq. (1)) was calculated. In this case study, the Pb and Sn ratios were not significantly affected by the chloride concentration (2 or 10 mg/L Cl) (Fig. 9). The Pb ratios for most of the conditions were between 1 and 4 and was as high as 12 for 120 mg/L as CaCO<sub>3</sub>, indicating that phosphate increased lead release in these test waters. The Sn ratios were higher than those calculated for lead and were between 1 and 10 in most cases, again indicating that tin was more affected by phosphate than lead (Fig. 9). Higher chloride (10 mg/L vs. 2 mg/L Cl) worsened the effect of phosphate on tin when the alkalinity was 5 mg/L as CaCO<sub>3</sub> or

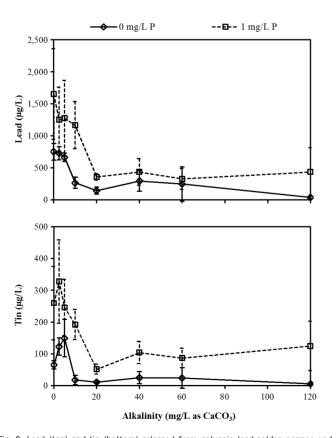


Fig. 8. Lead (top) and tin (bottom) released from galvanic lead solder-copper end caps as a function of alkalinity. The water contained 2 mg/L Cl, and the data points are average concentrations from the triplicates during Weeks 7 to 8. Error bars denote 95% confidence intervals.

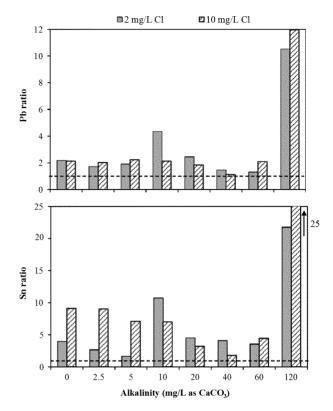


Fig. 9. Lead ratio (top) and tin ratio (bottom) for 2 and 10 mg/L Cl and alkalinity ranging between 0 and 120 mg/L as  $CaCO_3$ . The lead ratio was defined as lead release to water with phosphate divided by lead release without phosphate (Eq. (1)), and the tin ratio was the same formula but with tin release. The water contained no sulphate. Data for 2 and 10 mg/L Cl were from Weeks 7–8 and Weeks 5–6, respectively. The dashed line at a ratio of 1 indicates the level at which phosphate had no effect on lead or tin release.

less (Fig. 9), which is consistent with findings in Case Study 1 with low alkalinity water (Fig. 7). In summary, dosing 1 mg/L P significantly increased lead and tin release from soldered end caps in this case study, and the impact of orthophosphate was worse for tin. Additionally, higher chloride in low alkalinity water worsened the phosphate effect.

# 4. Conclusions

- (1) Dosing of orthophosphate occasionally creates significant adverse consequences on galvanic corrosion of lead bearing plumbing materials connected to copper tube. Because orthophosphate often has profound benefits in reducing lead release during uniform corrosion, the net impacts of orthophosphate on overall lead release to water in individual buildings (from sources including leaded brass, lead solder and lead pipe at various lengths) can be complicated.
- (2) The tendency toward adverse consequences of orthophosphate on galvanic corrosion of lead increased if the sulphate concentration was less than about 10 mg/L SO<sub>4</sub><sup>21</sup> or if the percentage of the current carried by SO<sub>4</sub><sup>21</sup> was less than 30%.
- (3) In cases where orthophosphate exacerbated galvanic corrosion of 50:50 Pb-Sn solder, tin release was more strongly affected than lead.
- (4) In certain waters, dosing orthophosphate increased the galvanic current and tin release from pure tin connected to copper pipe, which can be expected to reduce anode surface pH to a level where it cannot be passivated.

- (5) Consistent with prior work, phosphate had a more detrimental effect on corrosion of Pb-Sn solder at pH 7 than at pH 9.5 in one water tested.
- (6) Higher alkalinity did not mitigate the adverse effects of phosphate, but more lead and tin corrosion did occur at lower alkalinity.
- (7) Higher concentrations of chloride in low alkalinity water (<10 mg/L as CaCO<sub>3</sub>) also worsened the effects of phosphate on solder corrosion

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